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Formation of Hydrocarbons from Carbon Monoxide
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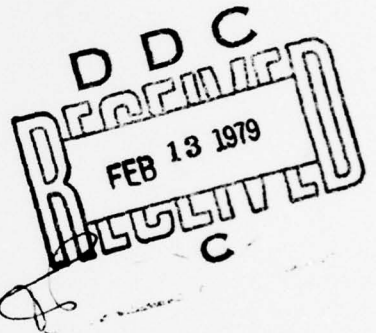
by

R.M. Kroeker, W.C. Kaska and P.K. Hansma

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University of California, Santa Barbara
Department of Physics
Department of Chemistry
Quantum Institute
Santa Barbara, CA

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Formation of Hydrocarbons from Carbon Monoxide
on Rhodium/Alumina Model Catalysts^{*}

R. M. Kroeker, W. C. Kaska, and P. K. Hansma[†]

Department of Physics (RK & PH) and Department of Chemistry (WK)

University of California, Santa Barbara, CA 93106

ABSTRACT

Adsorbed hydrocarbons are produced when tunnel junctions containing carbon monoxide chemisorbed on rhodium/alumina are heated. Two different species can be produced with different reaction conditions. Isotopic substitution with $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$, and reference to published spectra allow their identification as formate ions and an ethylidene species.

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[†]Alfred P. Sloan Foundation Fellow.

I. INTRODUCTION

The observation of catalytic intermediates on supported metal catalysts would enable one to describe the step-by-step formation of hydrocarbons from carbon monoxide. Many possible intermediates have been proposed,¹ but there is little spectroscopic information available to enable the determination of the correct reaction pathway for any given catalyst system. This study was carried out with the hope that tunneling spectroscopy might give new information about relatively stable surface species present during the hydrogenation of carbon monoxide. This work is a continuation of a previously reported tunneling spectroscopy study² of a model rhodium/alumina catalyst.

We report the observation of two surface species formed from chemisorbed carbon monoxide. One species consists of formate ions; the second is a two-carbon, four-hydrogen molecule that is multiply bonded to the rhodium, μ ethylidene dirhodium. These identifications are based on the measurement of isotopic shifts, and on comparison of mode positions to known compounds.

The formate species has been observed to form on ruthenium/alumina catalysts by others,³ and is not thought to be an active intermediate in hydrocarbon synthesis. The two-carbon species has not been observed previously on a supported metal catalyst. It forms under conditions more closely resembling those during practical hydrocarbon synthesis, and may be an intermediate in this synthesis. In a recent study by M. M. Bhasin, et al.,⁴ rhodium/ SiO_2 catalysts were shown to convert CO to C_2 chemicals with a 43% efficiency.

II. EXPERIMENTAL METHODS

The tunneling junctions used in these experiments are fabricated with a standard geometry; they consist of a thin aluminum film upon which an oxide is grown to form an insulating barrier, a dopant, and a lead top electrode. The details of the fabrication process and measurement techniques can be found in the literature.^{5,6}

The dopant for these experiments is a small amount of rhodium that is evaporated onto the oxidized aluminum⁷ and exposed to various gases. Prior to this evaporation the oxide surface is usually cleaned in an argon glow discharge. The rhodium is evaporated under varied vacuum conditions ranging from 3×10^{-6} Pa residual gases, mainly hydrogen and water vapor, to 1×10^{-2} Pa carbon monoxide. A typical evaporation is one in a pressure of 2×10^{-3} Pa of carbon monoxide. The carbon monoxide is left in the vacuum chamber for sixty seconds, then pumped out, and the top lead electrode deposited. This top layer of lead is normally 1500 angstroms thick.

We usually evaporate enough rhodium to equal a four to six angstrom uniform layer. The rhodium does not, however, form a uniform layer; instead, it lowers its surface free energy by balling up to form small particles with diameters on the order of twenty to thirty angstroms.⁸

In this work with supported rhodium, we are forced to deal with lower overall intensities than are produced by an organic monolayer. To aid in the detection of very small peaks, we take differential spectra by subtracting the signal of an undoped

junction from the spectrum of a doped junction.⁶ In every experiment, this undoped junction is formed next to the doped junction, so all spectra taken are the difference spectra of two junctions. The simultaneous formation of both junctions reduces subtraction problems associated with the variability of control, or undoped, junctions.

For the experiments with isotopes, $^{12}\text{C}^{18}\text{O}$ (99%) was obtained from Stohler isotopes, and $^{13}\text{C}^{16}\text{O}$ (90.5%) was obtained from Merck, Sharp, and Dohme. Both were used as received without further purification.

To produce hydrocarbons from the carbon monoxide present in the junctions, the junctions must be heated. At present, our best vacuum is not sufficient to heat an uncompleted junction without exposure to contaminating residual gases. To obtain hydrocarbons without such contamination, we first complete the junctions with a top lead electrode and then heat the completed junctions in a separate chamber. There are advantages and disadvantages inherent in heating completed junctions in a separate chamber. The main disadvantage is that it removes our model supported metal system another step from straightforward comparison to practical catalyst systems. The advantages include the following: (1) We can take spectra before and after we heat the junctions, and we can take successive spectra of the same junction after heating to increasing temperatures; (2) We can heat the junctions under high pressure; and (3) the lead acts as a mass selective filter to let through small reactants such as hydrogen while screening out hydrocarbon contamination.

To produce hydrocarbon spectra with good peak intensities we place a completed pair of junctions, one doped with rhodium evaporated in carbon monoxide and one undoped, in a small high pressure cell. We evacuate the cell, and then pressurize it with hydrogen and carbon monoxide. For the experiments with isotopes hydrogen alone is used. We use maximum tank pressure, typically 1×10^7 Pa. The effective pressure of gas present on the rhodium is not known. The cell is then heated to 390-430 K for times from twenty to sixty minutes to form the hydrocarbons. After cooling, the junction is removed and immersed in liquid helium to obtain a spectrum.

III. RESULTS

Figure 1 shows the differential spectra resulting from the heating of a completed pair of junctions to 440 K, for twenty minutes. The heating cell was evacuated during the heating. No hydrocarbon was observed to form on the junction without rhodium. The modes indicated in Figure 1 are ones that vary together in intensity from sample to sample. Spectra showing the growth of mode intensities of formate ions on alumina with increasing coverage have been published by Lewis, et al.⁹ The modes first visible at low coverage are also indicated in Figure 1. From the agreement in position observed, the species is identified as formate ions; it is not determined if these ions are bonded to rhodium or alumina, or both.

The formation of formate ions on a supported metal catalyst has been observed previously. In experiments by Dalla Beta and Shelef,³ formate ions were observed to form on a ruthenium/alumina

catalyst. In a transmission infrared study with isotopes, they observed that the formate species was an inactive reaction product.

It is interesting to note that this reaction occurs in our junctions without the pressurization of the heating chamber. We have found that this species forms most readily in junctions prepared in a residual pressure of water vapor adequate to cover the surface during sample fabrication. The spectra of such junctions have OH stretching vibrations present. Junctions formed in a partial pressure of D₂O show a corresponding OD stretching vibration. Heating of the D₂O exposed junctions forms a deuterated hydrocarbon. The net reaction observed is thus the addition of an OH group to a CO molecule bonded to the rhodium. To inhibit the formation of this species, junctions are prepared in background pressures of water that are as low as is practical.

Figure 2 shows the spectra from a pair of junctions prepared in a background pressure of water vapor of 2×10^{-5} Pa, one-tenth that of Figure 1. During heating to 420 K it was exposed to 1×10^7 Pa of hydrogen. Although the formation of formate ions cannot be ruled out, it is clear that a new species has formed. The modes of this new species are labeled by integers in the figure. This hydrocarbon forms at temperatures as low as 380 K and appears to desorb at temperatures higher than 430 K. No hydrocarbon forms on the junction without rhodium.

To aid in the identification of this species, isotopic substitution of the carbon monoxide was used. Many shifts were seen with ¹³C¹⁶O, but no shifts were seen with ¹²C¹⁸O. This demonstrates the formation of a hydrocarbon without oxygen from the carbon monoxide on the rhodium particles. It is important that

no modes involving the oxygen from the chemisorbed carbon monoxide are observed. Many proposed intermediates involve a carbon-oxygen bond of some type. The group -CH=O , one possible intermediate, would have an oxygen-carbon mode between 190 to 220 meV, that is not seen. Such an oxygen-carbon bond formed from the carbon monoxide would have an easily observed isotope shift with $^{12}\text{C}^{18}\text{O}$ of 3 to 4 meV.¹⁰ Other oxygenated species, such as $\text{-CH}_2\text{OH}$ would also have an isotope shift large enough to be seen in the carbon-oxygen mode.¹⁰ We are not observing an oxygenated species. No mode in the region from 125 meV (1000 cm) to 180 meV (1440 cm) shifts with the use of $^{12}\text{C}^{18}\text{O}$.

The lack of intensity makes precise measurements of the observed shifts with $^{13}\text{C}^{16}\text{O}$ difficult. Uncertainties in shift magnitudes are large enough to prevent mode assignments without reference to additional data. However, all shifts measured are consistent with the mode assignments we make, and are discussed individually below.

The presence of the mode at 170.8 meV, mode five in Figure 2, is characteristic of a methyl group bonded to another carbon atom. This mode is the symmetric deformation of a CH_3 group, and is sensitive to the bonding of the carbon atom. With ^{13}C substitution this mode is expected to downshift about 1.0 meV.¹¹ We measure -1.4 ± 0.4 meV. The mode at 181.4 meV, mode six in Figure 2, is then identified as the antisymmetric deformation of the CH_3 group. Its expected shift is -0.7 meV.¹¹ We observe a shift of -0.4 ± 0.4 . The only other CH species with a vibration in this position is the CH_2 group. We do not see any other modes due to a CH_2 group; we

do see other modes due to a CH_3 group. There is no other CH group that will have modes in this region, and the isotope shift measurements do not allow the assignment of either of these modes as carbon-carbon or carbon-oxygen modes. Thus there is little doubt about the assignments of modes five and six.

Knowing that the hydrocarbon contains a CH_3 group, there is only one possible one-carbon species, RhCH_3 . Figure 3 shows a comparison of mode positions of X-CH_3 for $\text{X} = \text{bromine}$ and iodine with the species of Figure 2. The mode positions for the three species have been displaced by the inverse root of the mass of X . It can be seen that the species X-CH_3 has too few modes to be correct. The two modes that do agree are modes one and six. Mode one is in the position for a Rh-C bond. Mode six, the asymmetric deformation of a CH_3 group, is known to be insensitive to the bonding of the carbon atom; thus this agreement is expected. As mentioned previously, mode five is sensitive to the bonding of the carbon atom; it is seen to be downshifted in Figure 3 for both the bromine (1332 cm) and iodine (1276 cm) species.

The possible two-carbon species that contain a CH_3 group are: (a) RhCH_2CH_3 , (b) Rh_2CHCH_3 , and (c) Rh_3CCH_3 . The three-hydrogen species, c, does not have enough CH modes between 100 meV (800 cm) and 200 meV (1600 cm) to be the correct species. The five-hydrogen species, a, is represented in Figure 3 by XCH_2CH_3 for $\text{X} = \text{bromine}$ and iodine .¹³ This molecule correctly matches modes five and six, due to the terminal CH_3 group. But the modes due to the CH_2 group, as mentioned previously, are absent. Specifically, we do not observe a mode near 92 meV (790 cm). This

species also has too few modes between 100 and 200 meV. The four-hydrogen species, b, is represented in Figure 3 by X_2CHCH_3 for X = bromine and iodine.¹⁴ It is seen that the modes agree both in number and position. Perfect agreement in mode positions is not expected; we have not made any corrections for bonding differences between a halogen and a rhodium atom. This agreement in mode positions indicates that the hybridization of the carbon atoms in the tunneling junctions are the same as in the halogen compounds, sp^3 . The lack of a large shift in the position of mode one, after accounting for the mass effect, also indicates that this force constant is largely determined by the carbon atom. The close agreement observed in all mode positions allows the assignment of the modes of Figure 2 from assignments in the literature for Br_2CHCH_3 . They are as follows: mode one is a rhodium-carbon stretch for a bridged bonded carbon atom; mode two is a CH_3 rocking mode, doubly degenerate; modes three and four are CH deformations; modes five and six are CH_3 deformations; and mode seven contains the symmetric and antisymmetric CH_3 stretching, and CH stretching vibrations.

Two modes labeled A and B that are shown in Figure 3 are not numbered in Figure 2. The lowest of these, at 60 meV, is not labeled in Figure 2 due to the presence of the Rh-C=O bending mode near 58.1 meV. The mode in Figure 2 near this position is at 59.6 meV, upshifted 1.5 meV. This upshift increases with subsequent heating of the junctions. The growth of a new peak near 60 meV due to the formation of the hydrocarbon could explain this shift. The second mode that is not numbered in Figure 2 is the

mode at 117 meV, labeled as Al_2O_3 . We are unable to measure this mode position very accurately due to interference from the very strong aluminum oxide mode in this position. Subtraction errors lead to baseline shifts of the same order of magnitude as this peak. As a result of this interference, the isotope shift measured, 3 meV, has a large uncertainty, ± 3 meV. A carbon-carbon bond would be expected to downshift about 4 meV in this molecule.

Molecules with more than two carbon atoms have, in general, too many modes to be the correct species. One exception to this is the three-carbon species 2-X propane.¹⁵ The degeneracy of the CH_3 modes, only slightly split, yields a spectrum with the correct number of strong modes in the 100 to 200 meV (800 to 1600 cm) region. Mode position agreement, however, is weakened for the CH modes three and four, reflecting the change in bonding of this carbon atom. Mode position agreement is lost entirely for both mode one and the mode at 117 meV, reflecting the additional mass of the second CH_3 group. Thus we conclude that we are not seeing molecules with more than two carbon atoms.

To summarize our identification: (1) The lack of shifts with $^{12}\text{C}^{18}\text{O}$ and the lack of some characteristic modes show that the unknown does not contain oxygen. (2) A detailed comparison of observed peak positions for the unknown with all possible one-, two-, and three-carbon species shows agreement only for X_2CHCH_3 . Measured isotope shifts with $^{13}\text{C}^{16}\text{O}$ are consistent with this agreement. A similar species has recently been reported to form on the Pt(111) surface from the chemisorption of ethylene.¹⁶ It has been identified by Kesmodel, et al.,¹⁷ as an ethylidyne species, Pt_3CCH_3 .

Our observation of an ethylidene species with our model catalyst system suggests a reaction pathway that involves an oxygen free intermediate. One reaction pathway that is consistent with the experimental results is the formation of Rh_2C , as in the reaction $\text{Rh}_2\text{CO} + \text{CO} \rightarrow \text{Rh}_2\text{C} + \text{CO}_2$. With this as the rate limiting step, a junction heated in H_2 would then rapidly form methane. The observed hydrocarbon, Rh_2CHCH_3 , could then be formed from the reaction $\text{Rh}_2\text{C} + \text{CH}_4 \rightarrow \text{Rh}_2\text{CHCH}_3$.

Clearly many unanswered questions remain. Is this species an intermediate in practical hydrocarbon synthesis? What product distribution would be expected from a reaction pathway that included this as a (relatively) stable intermediate? Will this same species be found on other supported metals with different product distributions?

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FIGURE CAPTIONS

- Fig. 1. Differential spectra of CO on rhodium/alumina that has been heated to 440 K without hydrogen. New modes appearing upon heating are indicated by bars. Corresponding positions from low coverage formate ion spectra taken from the literature⁹ are shown at the bottom of the figure. The new species is thus identified as formate ions.
- Fig. 2. Differential spectra of CO on rhodium/alumina that has been heated to 420 K in hydrogen. New modes due to hydrocarbon formation are numbered 1 to 7. By comparison to published infrared and Raman spectra the hydrocarbon is identified as an ethylidene species.
- Fig. 3. Comparisons are shown between mode positions of the unknown hydrocarbon and positions from the literature¹²⁻¹⁴ of known compounds. The vertical axis is scaled by the inverse square root of the mass of Bromine, Rhodium, and Iodine. It is displaced for each set of compounds. Modes 1 to 6 of the unknown are observed directly. The measurement of the positions of modes A and B is difficult due to overlap with other modes present in Fig. 2. From the agreement shown with the two ethylidene species, the unknown hydrocarbon is identified as a μ ethylidene species, specifically 1,1 dirhodioethane.

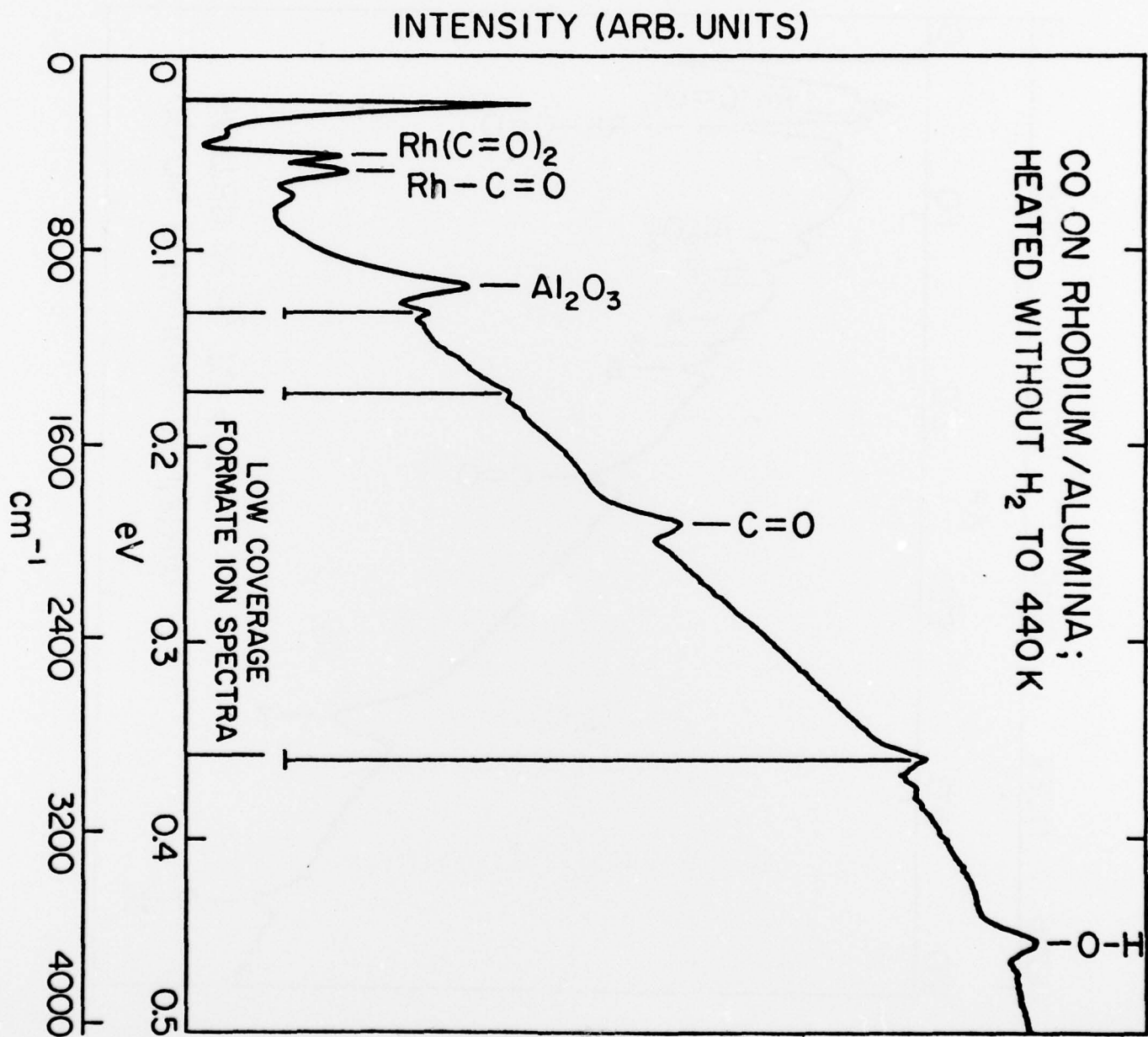


FIG. 1

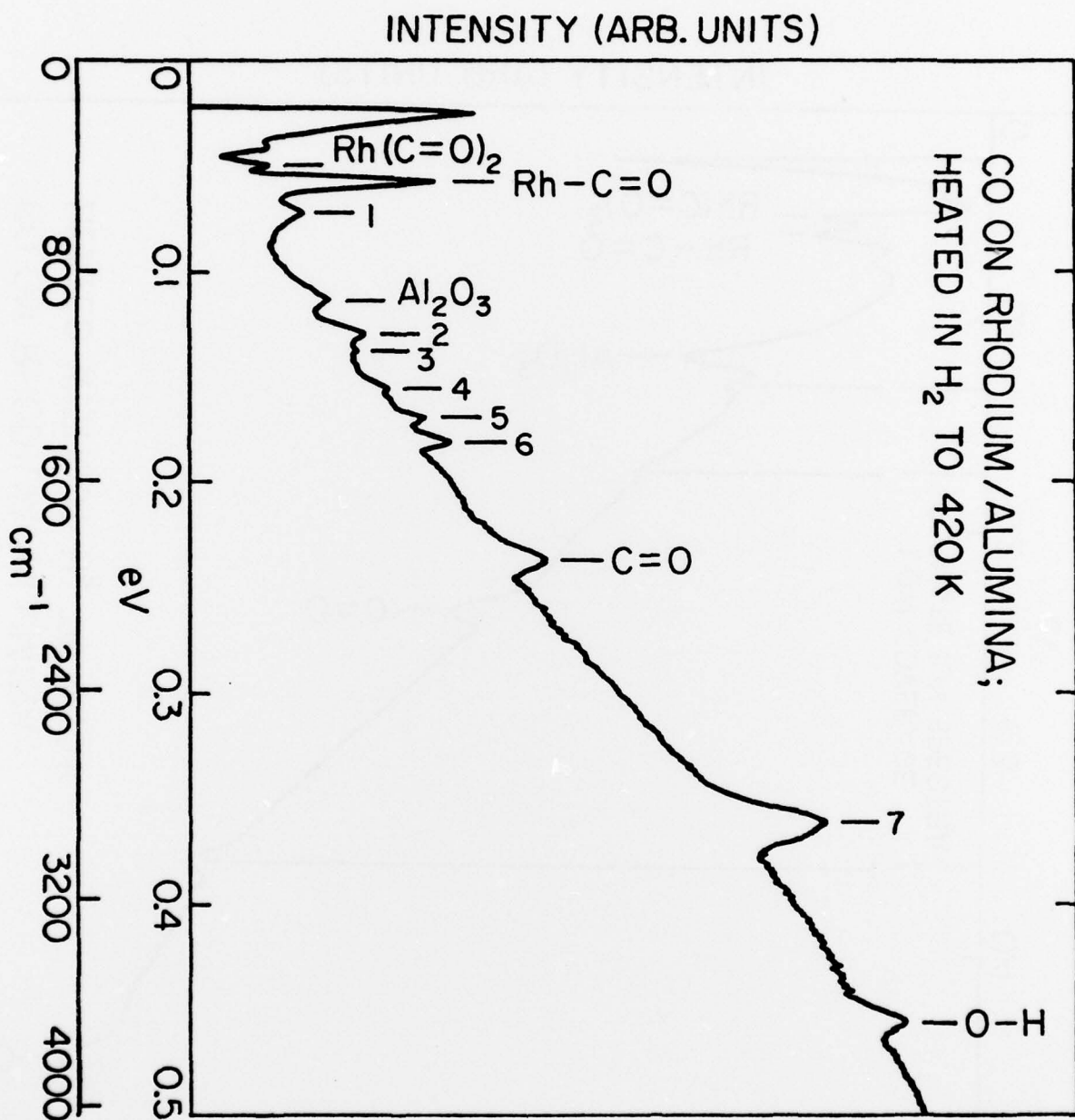


FIG. 2

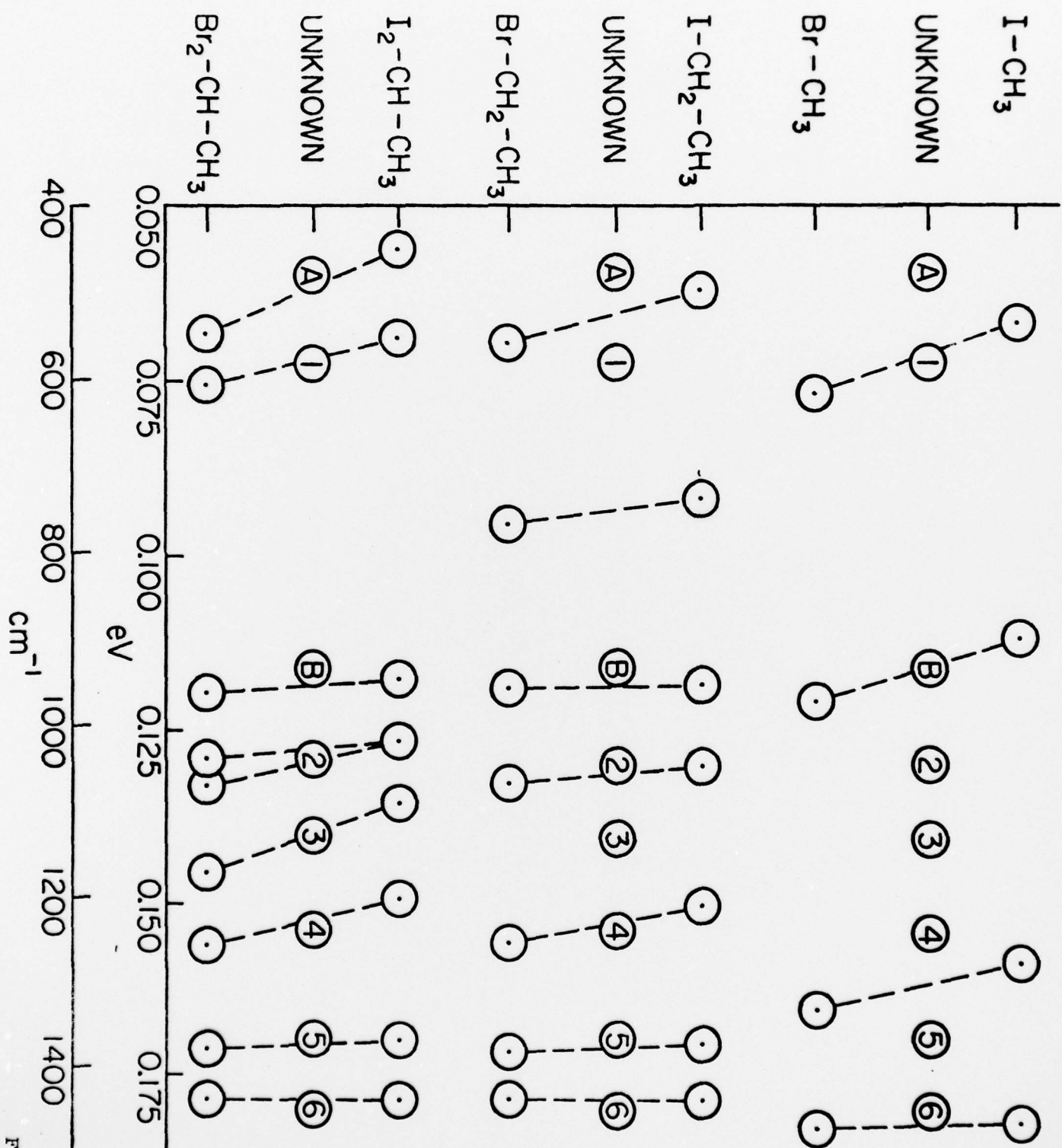


FIG. 3